

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 323 142 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **08.09.93** (51) Int. Cl.⁵: **C08L 71/00, C08L 79/08, C08L 83/06, H01B 3/30**

(21) Application number: **88312187.3**

(22) Date of filing: **22.12.88**

The file contains technical information submitted after the application was filed and not included in this specification

(54) **Ternary blends as wire insulations.**

(30) Priority: **24.12.87 GB 8730130**
20.04.88 GB 8809274

(43) Date of publication of application:
05.07.89 Bulletin 89/27

(45) Publication of the grant of the patent:
08.09.93 Bulletin 93/36

(84) Designated Contracting States:
BE DE ES FR GB IT NL

(56) References cited:

EP-A- 0 095 174	EP-A- 0 163 464
EP-A- 0 254 488	EP-A- 0 266 595
DE-A- 3 813 321	US-A- 4 250 279

(73) Proprietor: **PIRELLI GENERAL plc**
40 Chancery Lane
London WC2A 1JH(GB)

(72) Inventor: **Alesbury, Colin Kevin**
3 Forest Gate Mapley
Southampton Hampshire SO4 1GW(GB)
Inventor: **Murphy, Richard John, Dr.**
26 Saker Street
Liverpool(GB)

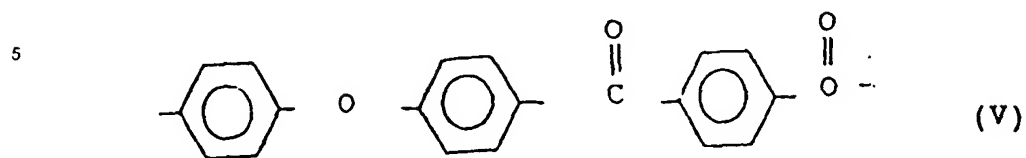
(74) Representative: **West, Alan Harry et al**
R.G.C. Jenkins & Co. 26 Caxton Street
London SW1H 0RJ (GB)

Property of:
Loctite Aerospace
R&D Technical Library
Return to library for filing when done.

Copyright fees paid. Further
copies require compliance with
copyright restrictions.

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

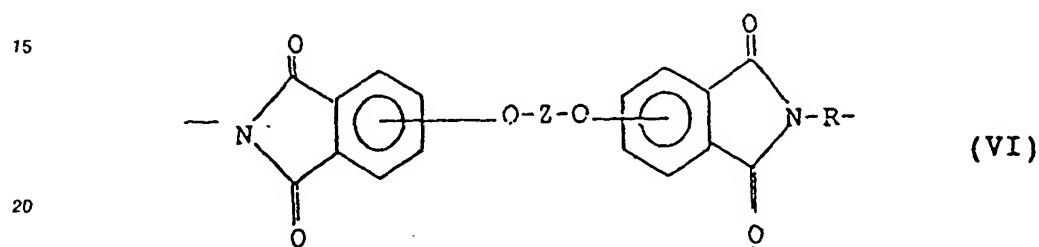
and the polyether ketone suitably contains repeating units of the general formula



10

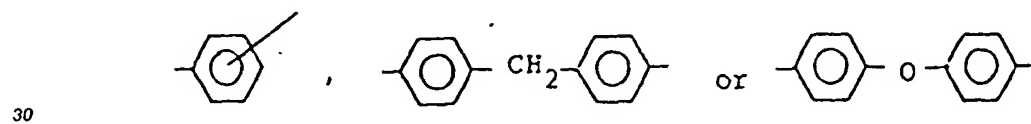
in which in all cases (III) to (V) the phenylene groups may carry one or more substituents.

The polyetherimide will generally contain repeating units of the general formula



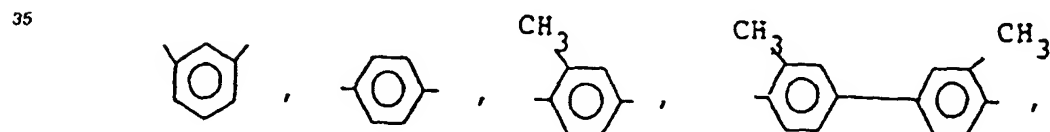
in which Z and R are organic groups, for example in which R is

25

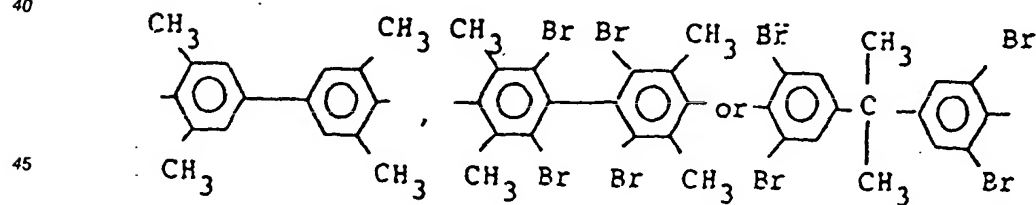


Z is

35



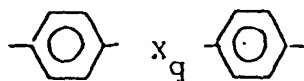
40



45

or a group of the formula

50



55

in which X is C_yH_{2y} .

(as is the case with polyethylenes) after the addition of a sensitiser, for example triallyl isocyanurate (TAIC) and N,N-metaphenylene dimaleimide (such as that available as HVA-2 from Du Pont), by irradiation.

The blends according to the invention have excellent resistance to environmental stress crazing in halogenated solvents and aviation fuel, and exhibit improved flexibility and flame retardance compared to PEEK alone.

These properties, in conjunction with good abrasion resistance, low toxic fume emission and smoke evolution, little or no halogen content and a wide temperature range of operation enable the use of the blends in high performance electronic and electrical wiring applications such as aircraft, ship and vehicle electrical systems, mass transit systems and high temperature equipment, as a single layer insulation or as the inner and/or outer layer of a double layer insulation.

Blending may be carried out at an elevated temperature for example from 300 to 400 °C, for example in a twin screw mixer. A range of useful blends may be obtained in this manner containing from 5 to 95% by weight PEEK or PEK, from 5 to 95% by weight PEI and up to 80% by weight S-PI, based on the blend. However, when the blend is to be used as a single layer insulation, then the PEEK content of the blend is preferably at least 45% by weight.

As described below in greater detail, blends according to the invention have been tested according to Defence Standard 61-12 (Part 18) Issue 2 and it has been found that blends containing from 45 to 95% by weight PEEK and up to 54% by weight PEI/S-PI comply with that standard. A preferred composition in this respect contains, by weight, 60% PEEK, 5% PEI and 35% S-PI.

Suitable materials for use in the blends of the invention include the PEEK material available from ICI under the trade name "Victrex", the PEK material available from Hoechst Plastics under the trade name "Hostatec" and the PEI and S-PI materials available from General Electric Plastics and General Electric Silicones under the trade names "Ultem" and "Siltem", respectively.

By way of illustration of the invention, a number of PEEK/PEI/S-PI blends were prepared and each was coated onto a tinned copper conductor by extrusion. The resulting wires were tested and found to comply with Defence Standard 61-12 (Part 18) Issue 2, as follows:

TABLE 1

Critical Oxygen Index (clause 8.2.7)			
composition (weight %)			oxygen index, %
PEEK	PEI	S-PI	Specification limit, 29%
15	15	70	50
20	20	60	51
25	25	50	48
50	25	25	53
70	15	15	41

[illegible]

TABLE 5

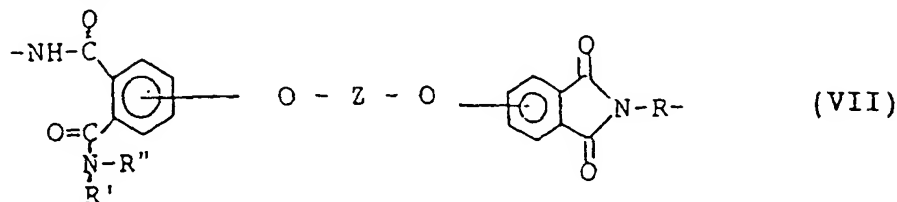
Composition (by weight)

Composition (by weight)	2:100	5:100	10:100	25:100	50:100	100:100	100:50	100:25	100:10	100:5	100:2
Ultem/Siltem											
Ethylene glycol	PASS	PASS	FAIL	PASS	PASS	PASS	PASS	PASS	FAIL	FAIL	FAIL
Trichloroethane	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL
Isopropanol	PASS	PASS	PASS	PASS	PASS	FAIL	PASS	FAIL	PASS	FAIL	PASS
Phosphate Ester Based OX20	FAIL	FAIL	PASS	PASS	FAIL	PASS	PASS	PASS	PASS	PASS	PASS
Petroleum Based OM18	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
70% Isooctane/Toluene	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL	FAIL
DERV	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Synthetic OX38	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Deionised Water	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Sea Water	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS

55 Claims

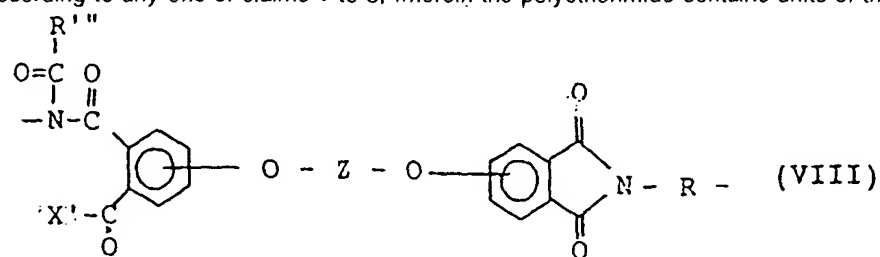
1. A blend comprising a poly(arylene ether ketone) together with a polyetherimide and a silicone-polyimide copolymer.

8. A blend according to any one of claims 1 to 7, wherein the polyetherimide contains units of the formula



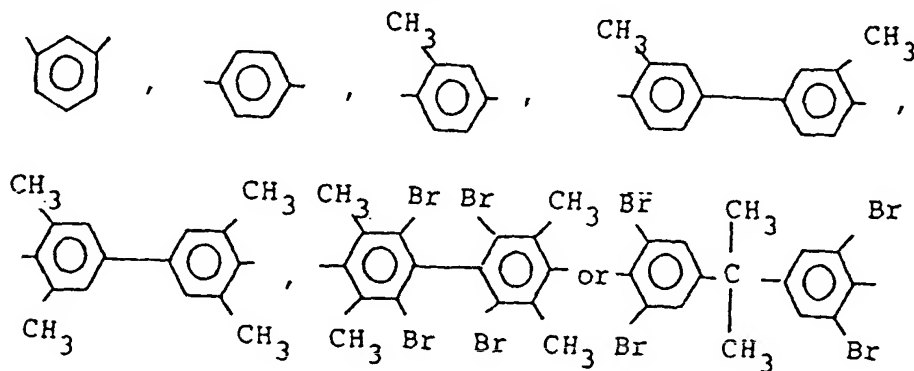
10 in which Z and R are organic groups, R' is an alkyl, alkenyl, alkoxyalkyl, ketyl, ketenyl, fluoroalkyl or fluoroalkenyl group having at least 4 carbon atoms, or is a phenyl or substituted phenyl group, and R'' is hydrogen or together with R' and the nitrogen forms an alicyclic group, obtainable by reacting a polyetherimide as specified in claim 7 with an amine of the formula R'-NH-R''.

- 15 9. A blend according to any one of claims 1 to 8, wherein the polyetherimide contains units of the formula

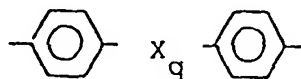


30 in which Z and R are organic groups, R'''CO is an acyl or fluoroacyl group having at least 4 carbon atoms and X' is a halogen, obtained by reacting a polyetherimide as specified in claim 7 with an acyl or fluoroacyl halide of the formula R'''CO-X'.

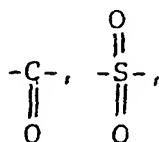
- 35 10. A blend according to any one of claims 7 to 9, wherein Z is

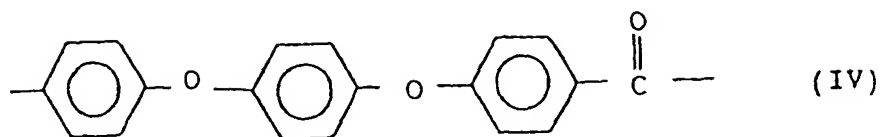


or a group of the formula



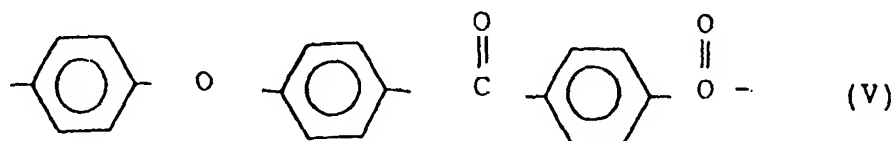
in which X is C_yH_{2y},





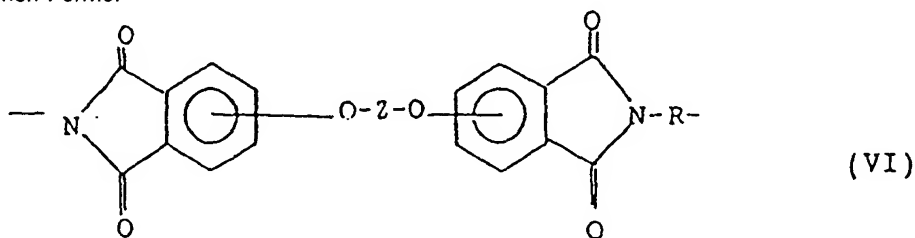
enthält, in denen die Phenylengruppen einen oder mehrere Substituenten tragen können.

6. Blend nach Anspruch 3, wobei das Polyetherketonketon Wiederholungseinheiten der allgemeinen Formel



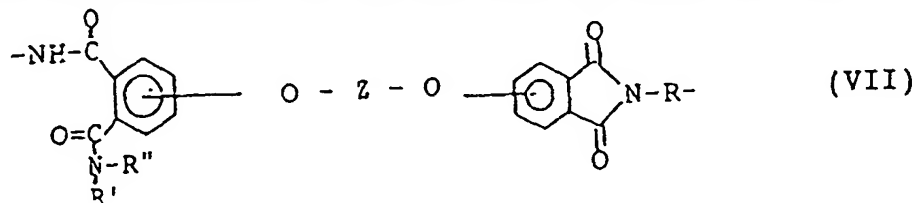
enthält, bei denen die Phenylengruppen einen oder mehrere Substituenten tragen können.

7. Blend nach einem der Ansprüche 1 bis 6, wobei das Polyetherimid Wiederholungseinheiten der allgemeinen Formel



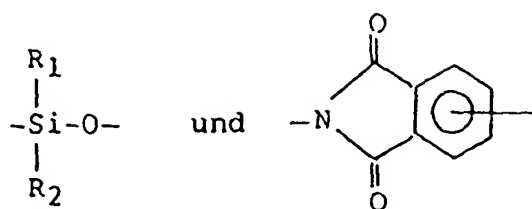
enthält, in der Z und R organische Reste bedeuten.

8. Blend nach einem der Ansprüche 1 bis 7, wobei das Polyetherimid Einheiten der Formel



enthält, in der Z und R organische Reste, R' einen Alkyl-Alkenyl-, Alkoxyalkyl-, Ketyl-, Ketenyl-, Fluoralkyl- oder Fluoralkenyl-Rest mit mindestens 4 Kohlenstoffatomen oder eine Phenyl- oder substituierte Phenylgruppe bedeutet und in der R'' die Bedeutung von Wasserstoff hat oder zusammen mit R' und den Stickstoffatomen einen alicyclischen Rest bildet, erhältlich durch Umsetzen eines Polyetherimids wie in Anspruch 7 spezifiziert mit einem Amin der Formel R'-NH-R''.

9. Blend nach einem der Ansprüche 1 bis 8, wobei das Polyetherimid Einheiten der Formel



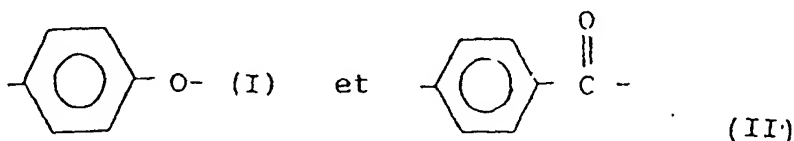
10 enthält, in denen R_1 und R_2 organische Reste bedeuten.

13. Geformter Gegenstand, enthaltend ein Gemisch gemäß einem der Ansprüche 1 bis 12.

15 14. Geformter Gegenstand nach Anspruch 13 in Form einer Einfachschichtisolierung oder als innere und/oder äußere Schicht einer Doppelschichtisolierung, die für einen elektrischen Leiter angewandt wird.

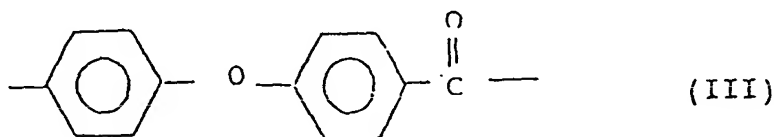
Revendications

- 20 1. Mélange comprenant une poly(aryleneéthercétone) avec un polyétherimide et un copolymère silicone-polyimide.
- 25 2. Mélange selon la revendication 1, dans lequel la poly(aryleneéthercétone) contient des unités de formules générales



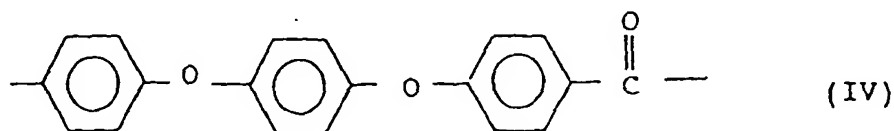
qui peuvent porter un ou plusieurs substituants sur les cycles arylène.

- 35 3. Mélange selon la revendication 1 ou la revendication 2, dans lequel la poly(aryleneéthercétone) est une polyéthercétone, une polyétheréthercétone ou une polyéthercétonecétone.
- 40 4. Mélange selon la revendication 3, dans lequel la polyéthercétone contient des unités constitutives de formule générale



dans laquelle les groupes phénylène peuvent porter un ou plusieurs substituants.

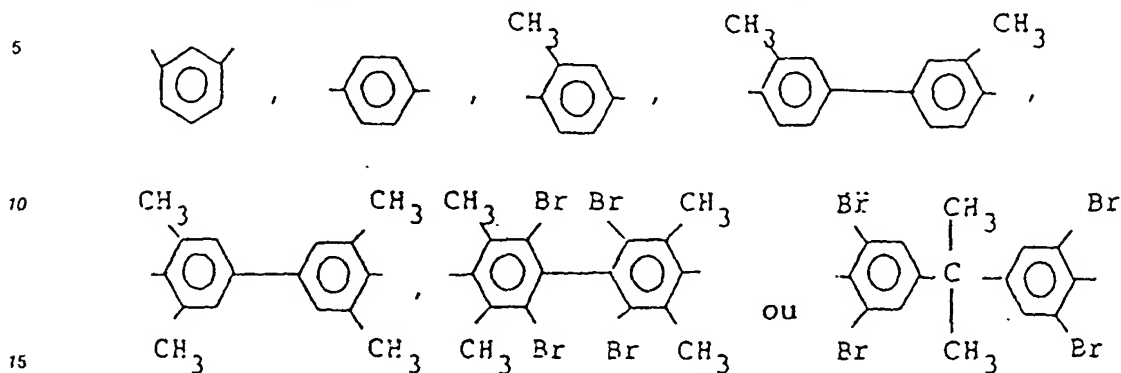
- 50 5. Mélange selon la revendication 3, dans lequel la polyétheréthercétone contient des unités constitutives de formule générale



dans laquelle les groupes phénylène peuvent porter un ou plusieurs substituants.

spécifié dans la revendication 7 avec un halogénure d'acyle ou de fluoroacyle de formule $R'''CO-X'$.

10. Mélange selon l'une quelconque des revendications 7 à 9, dans lequel Z est



ou un groupe de formule



dans laquelle X est C_yH_{2y} ,

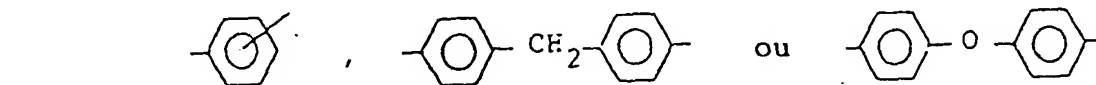


30

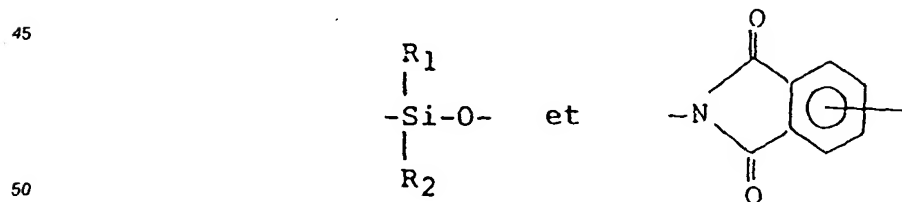
-O- ou -S-,

q est 0 ou 1 et y est un entier de 1 à 5, et les liaisons du groupe -O-Z-O- sont en position 3,3'; 3,4'; 4,3' ou 4,4'.

35 11. Mélange selon l'une quelconque des revendications 7 à 10, dans lequel R est



12. Mélange selon l'une quelconque des revendications 1 à 11, dans lequel le copolymère silicone-polyimide contient des groupes de formule



où R_1 et R_2 sont des groupes organiques.

55 13. Article moulé comprenant un mélange selon l'une quelconque des revendications 1 à 12.

14. Article moulé selon la revendication 13, sous forme d'un isolant en couche simple ou sous forme de la couche interne et/ou externe d'un isolant à deux couches, appliqué sur un conducteur électrique.